(12) UK Patent Application (19) GB (11) 2 302 687 (13) A

(43) Date of A Publication 29.01.1997

(21) Application No 9613019.0

(22) Date of Filing 21.06.1996

(30) Priority Data
(31) PN3880 (32) 29.06.1995 (33) AU

(71) Applicant(s)
Memtec Limited

(Incorporated in Australia)

1 Memtec Parkway, South Windsor, NSW 2756, Australia

(72) Inventor(s)
William Henry Alexander Pugh
Ralph Angelo Arruzza

(74) Agent and/or Address for Service
W P Thompson & Co
Celcon House, 289-293 High Holborn, LONDON, WC1V 7HU, United Kingdom

(51) INT CL[6]
C02F 1/50

(52) UK CL (Edition O)
C1C CACG C20X C200 C251 C253 C254 C31X C41Y C412

(56) Documents Cited
GB 2210362 A

(58) Field of Search
UK CL (Edition O) C1C CACG CRCG
INT CL[6] C02F
ONLINE: WPI

(54) Bromine stabiliser

(57) The present invention relates to a process for treating a water cooling circuit comprising concurrent or sequential steps of:
(1) liberating bromine from a bromine salt by means of a chlorine compound; and
(2) allowing the liberated bromine to react with an amine to form a bromamine.

GB 2 302 687 A

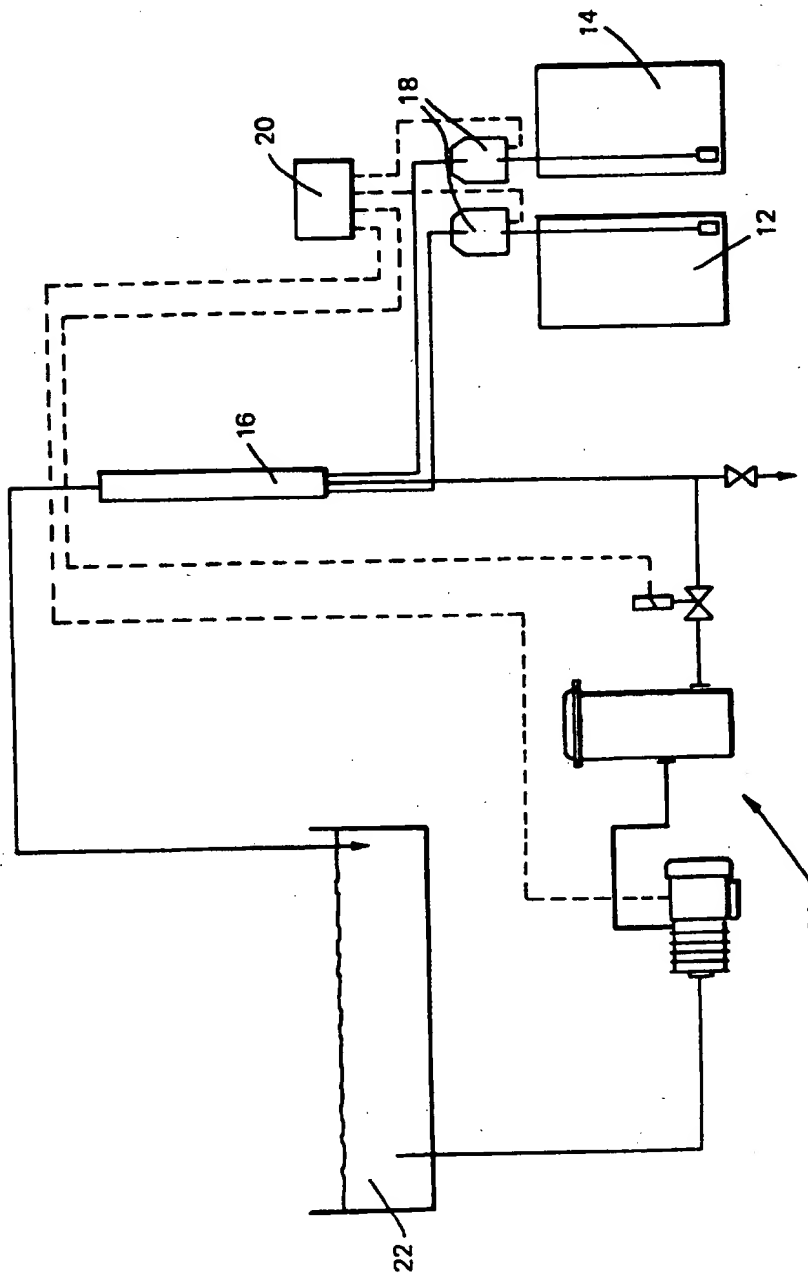


FIG. 1

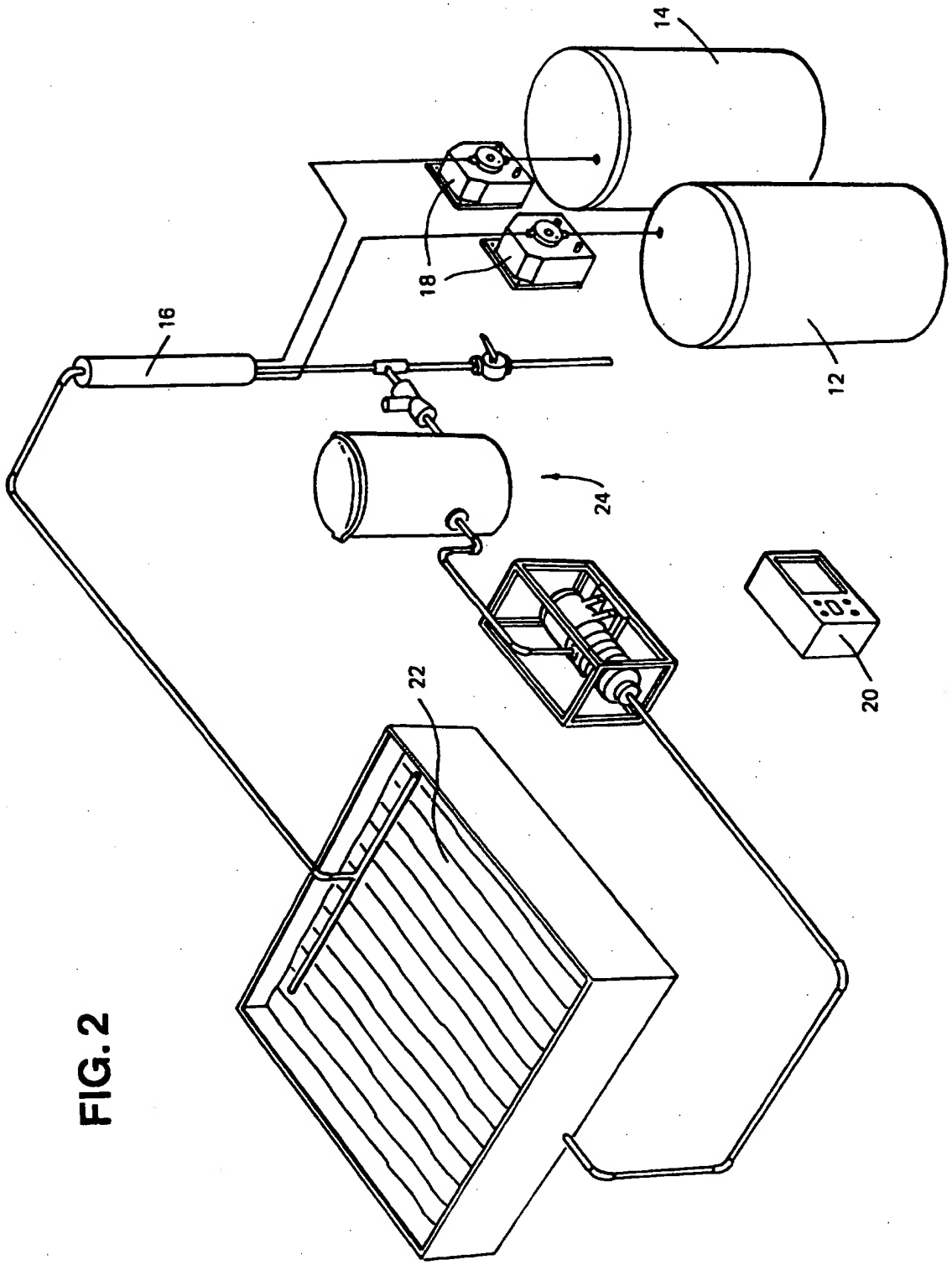
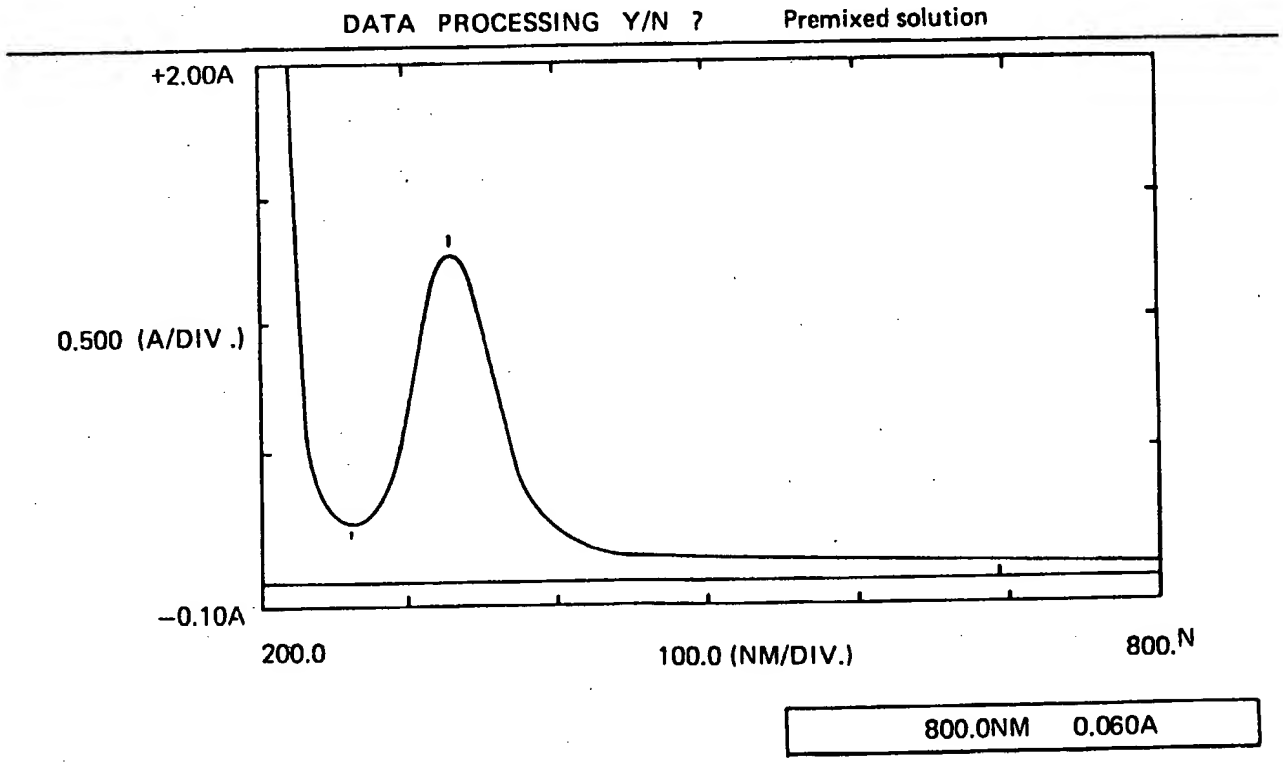


FIG.2

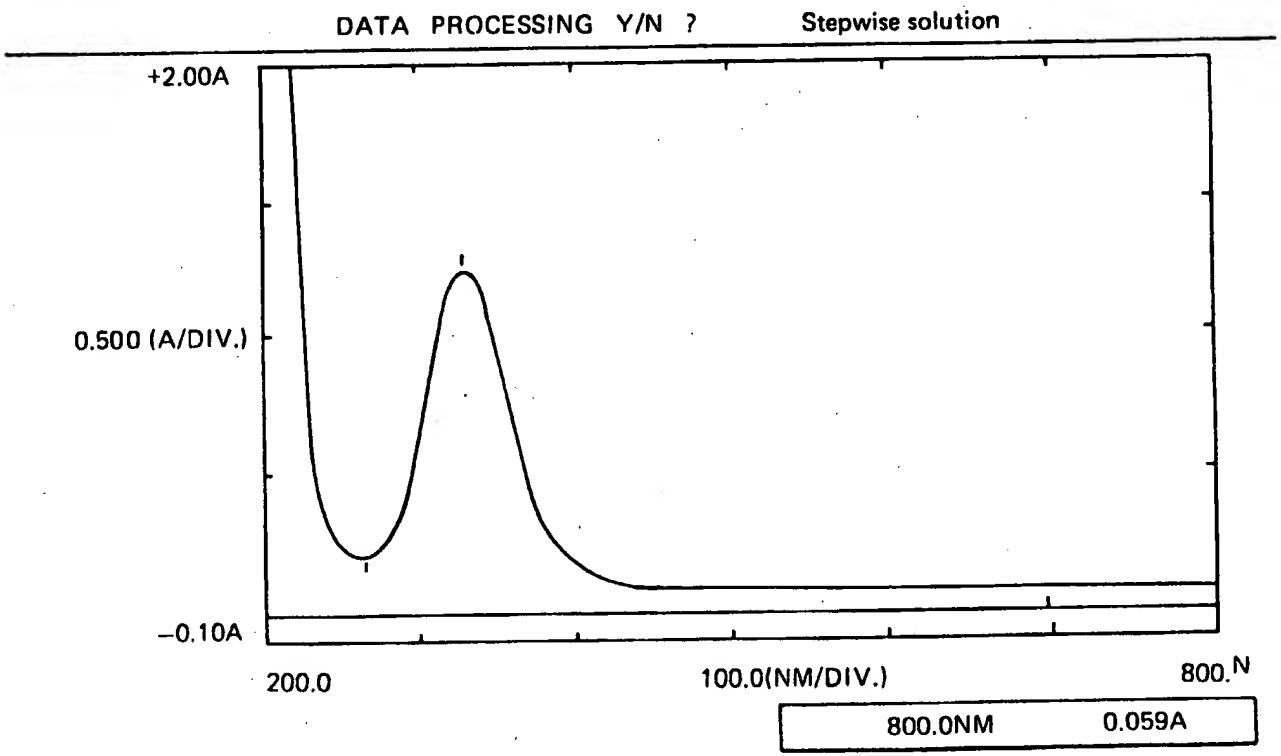
PEAK λ	PEAK ABS	VALLEY λ	VALLEY ABS
329.0	1.280	694.0	0.057
		261.0	0.223

FIG. 3



PEAK λ	PEAK ABS	VALLEY λ	VALLEY ABS
329.0	1.246	696.0	0.055
		265.0	0.207

FIG. 4



BROMINE STABILIZER

The present invention relates to a process for treating water cooling circuits and, in particular, to a process for treating water cooling circuits using stabilised bromine. The invention has been developed primarily for use in the treatment of water cooling circuits and will be described hereinafter with reference to this application. However, it will be appreciated that the invention is not limited to this particular field of use.

A particular antimicrobial agent or biocide for a system such as a water cooling circuit is usually chosen after consideration of a number of criteria including a biocide's ability to combat the microorganisms of concern to the degree desired; its physical and chemical compatibility with the system; its ability to remain stable in use and under storage conditions for extended periods of time; and its non toxicity.

The pH of water cooling circuits typically ranges between 8.3 and 8.5. Therefore the choice of biocide for treatment of such systems is limited to those which are able to effectively operate at high pH levels.

Bromine, in its hydrolysed form of hypobromous acid or HOBr is a biocide commonly employed in the treatment of water cooling circuits. This compound is used in preference to many other compounds such as chlorine or hypochlorous acid as it is physically and chemically compatible with the system particularly at high pH levels. That is unlike hypochlorous acid, the dissociation curve for hypobromous acid is at a higher pH which means that the availability of hypobromous acid is not pH dependent and dissociation will not occur at normal cooling circuit pHs. It has been found that hypobromous acid is approximately five times more effective than hypochlorous acid at these pH levels.

Further, the control and effectiveness of hypobromous acid as a biocide against organisms such as E. coli, Pseudomonas sp. and Streptococcus faecalis is superior compared with other biocidal agents such as hypochlorous acid and bromochlordimethyl hydantoin. Clearly, hypobromous acid had proven to be an effective biocide.

However, hypobromous acid has a number of disadvantages which have restricted its use. In particular hypobromous acid is an unstable form of bromine and is corrosive to metals such as mild steel. This has meant that this biocide cannot be retained in the cooling circuit for extended periods of time.

It is therefore an object of this invention to avoid or ameliorate at least some of the above discussed disadvantages.

According to a first aspect the present invention consists in a process for treating a water cooling circuit comprising concurrent or sequential steps of:

(1) liberating bromine from a bromine salt by means of a chlorine compound; and

(2) allowing the liberated bromine to react with an amine to form a bromamine.

Surprisingly, it has been found that the bromamines produced in situ provide substantial advantages over the prior art. In particular bromamine is as effective as hypobromous acid in terms of its biocidal abilities; has a longer half-life and is less corrosive to cooling system components.

In a preferred aspect, the bromine salt is sodium bromide in a concentration ranging from 5% to 45% w/v and the amine is monoethanolamine in an amount ranging from 2.8% to 25% w/v. Preferably the chlorine compound is a sodium hypochlorite having from 1.6% to 14% available chlorine. The actual percentages of each of the components will vary depending on the application of the process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention will now be more particularly described with reference to the following example and accompanying Figures. These are set forth by way of illustration and teaching only and ought to be construed as non-limiting on the scope of the present invention.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic diagram of the process of the present invention and the application of the bromamine to a water cooling circuit;

Figure 2 is a perspective view of the process of the present invention and the application of the bromamine to a water cooling circuit;

Figure 3 is a UV/Visible spectrograph of a resultant stabilised solution that was prepared by premixing sodium bromide and polyamine and then adding sodium hypochlorite; and

Figure 4 is a UV/Visible spectrograph of a resultant biocide solution that was prepared by stepwise mixing of sodium hypochlorite with sodium bromide and then adding polyamine.

EXAMPLE

As shown in Figures 1 and 2, for the treatment of water cooling circuits on a smaller scale, predetermined amounts of a 40% w/v aqueous solution of sodium bromide from tank 12 to which an amine has been added and a solution of sodium hypochlorite from tank 14 containing 12.5% available chlorine are applied to a reaction vessel 16, preferably a 3 inch cylindrical tube, using pumps 18 that are controlled by a duration and frequency timer 20. In reaction vessel 16 the reagents are mixed for a controlled period to give the following stoichiometric reaction:

$$NaOCl + NaBr \rightarrow NaOBr + NaCl$$

Typically, sodium hypochlorite is used in the treatment of water cooling circuits on a smaller scale as only a small amount of chlorine (approximately 10%) is required to liberate bromine. However, other chlorine compounds may be used including calcium hypochlorite and chlorine gas. In the treatment of a larger water cooling circuit such as a power station, it is preferable that chlorine gas is used as 100% chlorine is usually required to liberate bromine from the bromine salt.

The bromine salt used in the process of the present invention is typically sodium bromide, although other bromine salts may be used.

Following completion of the first stage of the reaction the amine then reacts with the bromide derivative to give bromamine. Depending on the pH in reaction vessel 16 the bromide derivative may exist as bromine, hypobromous acid or hypobromite ion. It has been found that amine reacts with bromide derivative in the same way as other nitrogen/hydrogen salts such as ammonia would react. That is

$$HOBr + NH_3 \rightarrow NH_2Br + H_2O$$
(monobromamine)

$$NH_2BR + HOBr \rightarrow NHBr_2 + H_2O$$
(dibromamine)

$$NHBr_2 + HOBr \rightarrow NBr_3 + H_20$$
(tribromamine)

Examples of the amine which may be used to produce bromamine in situ are preferably selected from the group consisting of monoethanolamine, quarternary amines and straight chain amines. In addition, it is possible that the breakdown of protein originating from dead bacteria in the cooling circuit may also be a source of amine.

The above procedure can be carried out either by stepwise mixing of sodium hypochlorite with sodium bromide and then the addition of polyamine or by premixing of sodium bromide with a polyamine and then the addition of a sodium hypochlorite. In both instances it was found that an hypochlorite-bromide reaction precedes the formation of halomines, resulting in bromamines. Thus the approach taken does not affect the composition of the final solution. This is clearly shown in the UV/Visible spectrographs of Figures 3 and 4 wherein the resulting solutions obtained following the use of both approaches were analysed using an ultraviolet/visible spectrophotometer over the range of 200-800nm. The resulting spectra are very similar; with both having a major peak at 329nm.

Surprisingly, it has also been found that the presence of chlorine with a mixture of sodium bromide and amine forms a bromamine in preference to chloramine.

Upon completion of the reaction, the resultant solution containing bromamine is applied to cooling circuit 22 by actuation of pumps 18 which are controlled by duration and frequency timer 20. Preferably an amount l ppm of free bromine equivalent is applied to the circuit every two hours..

Water from the cooling circuit 22 passes though reaction vessel 16 on a continuous basis to carry the discharged resultant stabilised disinfectant into circuit 22 whenever pumps 18 are activated by timer 20. A side stream filter generally designated 24 which is installed on the line supplying cooling water to reaction vessel 16 is used to provide "solid" free water to reaction vessel 16 and to clarify the recirculating cooling water. Up to 10% of the flow of cooling circuit 22 can be filtered which increases the tower cleanliness, by enhancing the effectiveness of the biocides and reduces the corrosive effects of sulphate reducing bacteria.

Disposable cartridge filters may be used for the purpose of removing any suspended particles of 20 micron or more. It has been found that even when the pores of the filter are reduced by fouling, the filter is still capable of removing smaller particles.

Preferably Diamond Filter Tube cartridges which are composed of wound polypropylene are used.

An alternative to the disposable cartridge filter is the sand filter backwash system. However, the cartridge filter system is used in preference to the sand filter backwash system as it is cheaper and the impurities removed are concentrated on the filter and are readily disposed rather than being backwashed to the sewer. In addition the use of the cartridge filter system saves on water usage.

Once in the water cooling circuit 22 the bromamines will either destroy all the microbes present or just prevent their further proliferation to numbers that would be significantly destructive to the system. More importantly bromamine can be retained continuously in the system as an effective biocide because they are less corrosive to cooling system components compared to other bromine derivatives such as hypobromous acid.

The above procedure can be effectively employed in the treatment of water cooling circuits on a larger scale. However the reagents of sodium bromide and amine are usually added straight into the circuit and chlorine gas is applied to the circuit in a predetermined dose.

The following efficacy trials illustrate the effectiveness of bromamines which are prepared by the process of the present invention. These trials are set forth by way of illustration and teaching only and ought to be construed as non-limiting on the scope of the present invention.

EFFICACY TRIALS

A disinfection programme was conducted in water cooling circuits at a number of sites in the Sydney area. NSW Health Department guidelines provide that Legionella spp. in the circuit must be less than 10 cfu/ml and the standard plate count must be less than 10^5 cfu/ml. The water cooling circuits at the various sites were treated according to the above Example. Bromamine was applied automatically by a timer controlled Brogard™ unit dosing rate of 1ppm/daily. Samples were taken on a monthly basis and analysed. The results shown in the Table I establish that bromamine is an effective biocide for the treatment of water cooling circuits.

Date of sampling (day #)	Date of previous biocide dose (day #)	Legionella spp. cfu/ml	Standard plate count cfu/ml
2	1	N/D	$8.1x10^4$
34	33	N/D	$1.1x10^4$
69	69	N/D	$1.0x10^2$
97	96	N/D	$1.2x10^4$
124	123	N/D	$3.8x10^4$
153	152	N/D	$7.7x10^3$
189	188	N/D	$5.1x10^4$
230	230	N/D	$1.0x10^2$
261	229	N/D	$1.0x10^6$
281	280	N/D	$6.0x10^4$
314	313	N/D	$2.9x10^5$

N/D = not detected

Although the invention has been described with reference to specific examples, it will be appreciate by those skilled in the art that the invention may be embodied in many other forms. In this regard it would be anticipated that the present invention could extend to other fields of application such as for the sanitation of circuits used for washing bottles in breweries etc.

CLAIMS

1. A process for treating a water cooling circuit comprising concurrent or sequential steps of :

(1) liberating bromine from a bromine salt by means of a chlorine compound; and

(2) allowing the liberated bromine to react with an amine to form a bromamine.

2. A process according to claim 1, wherein the bromine salt is a sodium bromide in a concentration ranging from 5% to 45% w/v and the amine is monoethanolamine in an amount ranging from 2.8% to 25% w/v.

3. A process according to claim 1 or claim 2, wherein the chlorine compound is selected from the group consisting of sodium hypochlorite, calcium hypochlorite and chlorine gas.

4. A process according to claim 3, wherein the chlorine compound is a sodium hypochlorite having from 1.6% to 14% available chlorine.

5. A process according to any one of the preceding claims, wherein the liberated bromine is in the form of a bromine derivative selected from the group consisting of bromine, hypobromous acid and hypobromite ion.

6. A process according to any one of the preceding claims, wherein the amine is selected from the group consisting of monoethanolamine, quarternary amines, straight chain amines and the breakdown of protein originating from dead bacteria in the cooling circuit.

7. A process according to any one of the preceding claims, wherein the steps are carried out sequentially.

8. A process for treating a water cooling circuit which process is substantially as herein described with reference to any one of the Examples and/or accompanying Figures.

The Patent Office

9

Application No: GB 9613019.0
Claims searched: 1-8

Examiner: Roy Honeywood
Date of search: 9 September 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C1C (CACG CRCG)

Int Cl (Ed.6): C02F

Other: ONLINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB2210362A	Nalco Chemical Company - see particularly page 5 line 4-14	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.